

Thermal evolution of the full three-dimensional magnetic excitations in the multiferroic BiFeO₃

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The idea of embedding and transmitting information within the fluctuations of the magnetic moments of spins (spin waves) has been recently proposed¹ and experimentally tested.² The coherence of spin waves, which describes how well defined these excitations are, is of course vital to this process, and the most significant factor that affects the spin-wave coherence is temperature. Here we present neutron inelastic scattering measurements of the full three-dimensional spin-wave dispersion in BiFeO₃, which is one of the most promising functional multiferroic material³, for temperatures from 5 K to 700 K. Despite the presence of strong electromagnetic coupling, the magnetic excitations behave like conventional magnons over all parts of the Brillouin zone. At low temperature the spin-waves are well-defined coherent modes, described by a classical model for a G-type antiferromagnet. A spin-wave velocity softening is already present at room temperature, and more pronounced damping occurs as the magnetic ordering temperature $T_N \sim 640$ K is approached. In addition, a strong hybridization of the Fe 3*d* and O 2*p* states is found to modify the distribution of the spin-wave spectral weight significantly, which implies that the spins are not restricted to the Fe atomic sites as previously believed.

Coupling between static magnetic and ferroelectric orders in multiferroic materials has attracted tremendous recent interest because of its potential use in device applications.⁴⁻⁶ If such coupling were to extend to dynamical properties, e. g. between lattice vibrations and spin fluctuations, then a new type of excitation may emerge. Such hybrid excitations, or “electromagnons,” have already been studied in a number of multiferroic systems using dielectric and Raman measurements.⁷⁻¹⁰ An even more fascinating aspect of this novel concept is the potential ability to control the spin waves using the electric fields generated by low-power dissipating electronic circuits instead of magnetic fields, a possibility that has been suggested for multiferroic BiFeO₃ at room temperature,^{10,11} making this material of particular interest³. Unfortunately optical measurements such as Raman scattering are only sensitive to long-wavelength ($q \sim 0$) excitations. Neutron scattering techniques, on the other hand, provides a powerful tool to probe these hybrid excitations over a large momentum space. There have already been some pioneering neutron scattering measurements on the magnetic excitations from powder BiFeO₃ samples¹², as well as single crystal samples^{13,14} but measured only around room temperature. A more complete pic-

ture of these modified spin-wave excitations, i. e. the electromagnons, at all wave vectors \mathbf{Q} , and especially their evolution with temperature is highly desired.

BiFeO₃ becomes ferroelectric at $T_C \sim 1100$ K. Below T_C this material exhibits an $R\bar{3}C$ ^{15,16} crystal structure, which can be viewed as a (weakly) rhombohedrally-distorted perovskite structure in which the oxygen octahedra are also distorted. For the purpose of our magnetic analysis this is well approximated by the pseudo-cubic unit cell shown in Fig. 1 (a). The Néel temperature for BiFeO₃ is $T_N \sim 640$ K, and the ordered magnetic phase has a cycloid modulation¹⁷ with a long periodicity that is superimposed on a simple G-type antiferromagnetic structure. The magnetic Bragg peaks appear close to the magnetic zone-centers of $\mathbf{Q}_{AF} = (0.5, 0.5, 0.5)$ (r.l.u.).

In Fig. 2 (a)-(d), the magnetic excitations measured at $T = 5$ K along [001], [110], [111], and [210] directions are plotted. At base temperature, the spin-wave excitations are well defined, and disperse quickly when moving away from \mathbf{Q}_{AF} . One will see that although the features at higher energies near the top of the bands are very well resolved, fine features at low energies for \mathbf{Q} near \mathbf{Q}_{AF} cannot be accurately determined, due to our relatively coarse energy and wave-vector resolution. We then choose to model the magnetic Hamiltonian by ignoring the effect of the long-period cycloid modulation, or any single-ion spin anisotropy in this system, which would only affect^{13,14} the magnetic excitations at low energies and in a narrow range around $\mathbf{Q}_{AF} \pm \delta$, where $\delta \sim 0.004$ along $\langle 110 \rangle$ are the modulation wave-vectors for the cycloid structure¹⁸. The Heisenberg spin Hamiltonian of the system therefore can be simplified to that of a classical G-type AFM, $H = J \sum_{n,m} \mathbf{S}_n \cdot \mathbf{S}_m$, where we only consider the nearest neighbor interaction J_1 , second nearest neighbor interaction J_2 , and the third nearest neighbor interaction J_3 , as shown in Fig. 1 (a). The interaction that dominates is clearly the nearest-neighbor exchange interaction J_1 between Fe spins separated along the $\langle 100 \rangle$ direction, whose magnitude can be roughly estimated from the top of the magnetic dispersion band, while J_2 and J_3 can also be obtained if the full dispersion is known (see Methods section for details). We have performed an overall fitting to our data using the model described in the Methods section to determine the exchange constants. The model calculations are shown in Fig. 2 (e)-(h), with fitting parameters shown in Table I. The calculated dispersion curves are also plotted in Fig. 2 as solid lines. It is apparent that our model provides a good description to the data at 5 K.

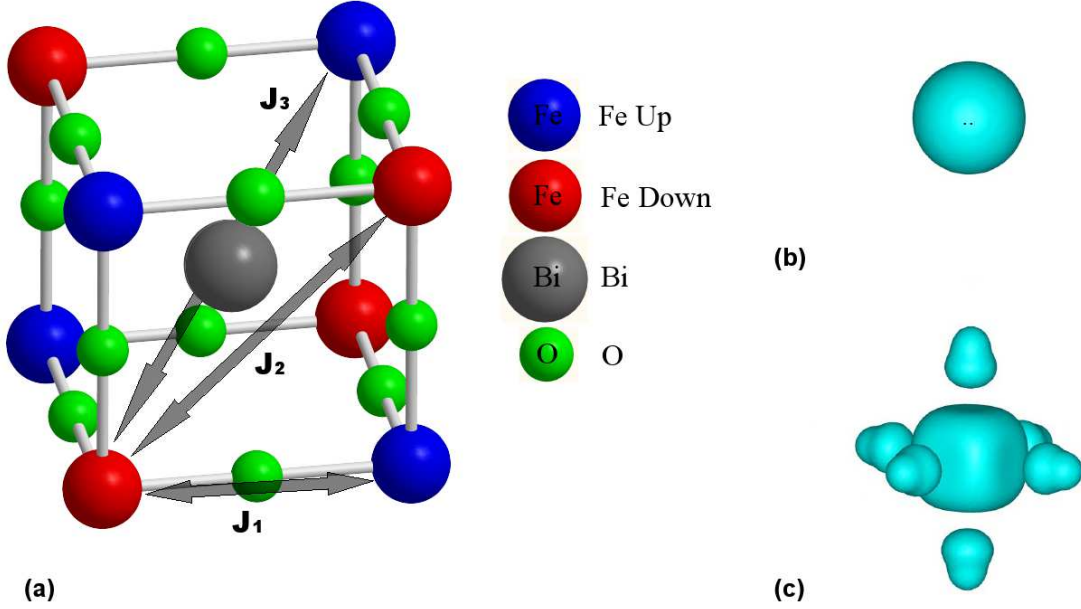


FIG. 1. (Color online) Schematics of the BiFeO₃ crystal structure (a), and spin densities from conventional Fe ionic model (b) and from first principles Wannier analysis taking into account the O 2*p* orbital (c).

The fact that J_1 , J_2 and J_3 are all positive, suggests that there is frustration in the system. Specifically, the face-diagonal Fe-Fe spins are aligned along the same direction in spite of the fact that the interactions between them are antiferromagnetic.

Upon heating the spin-wave is modified gradually. The intensity of low energy magnetic excitations is boosted by the Bose factor from 5 K to 140 K and then 300 K, while the overall shape still remain unchanged [see Fig. 3 (a) - (c)]. This is expected and can be understood as intensities from the magnetic Bragg peak are shifted into the inelastic channels when the static order becomes less robust with heating. At higher energies near the band top, the change is minimal between 5 K and 140 K, but at 300 K the band top is noticeably lower [Fig. 3 (c)], and the excitations become broader in energy. The softening of the spin-wave modes is due to the renormalization that occurs at non-zero temperatures, which is essentially a result of interactions between the excited magnons, and can be modeled with various theories. Instead of going into details of the renormalization, we would still use the same simple spin-wave model that describes the low-T data well, but with a set of renormalized effective exchange parameters shown in Table I. At 140 K the effective exchange parameters are virtually the same as those obtained at 5 K. The effective exchange constants J_1 and J_2 both show a clear drop at $T=300$ K, and a broadening in energy of $\Gamma \sim 5$ meV is required to obtain a good fit to the data. Our results indicate that although the spin-waves are still relatively well defined at room temperature, the lifetime (inverse of the energy width) of the spin-wave mode does decrease significantly compared to that at base tempera-

ture. The magnitude of the spin-wave softening is smaller than the softening observed of the electromagnon modes⁸ by Raman measurements near $q = 0$, but note that the energy of the $q = 0$ mode in the Raman work is also related to the cycloid wave-vector¹⁹ δ , which also drops with heating¹⁸. The clear spin-wave velocity softening at 300 K makes the low temperature measurements important to obtain the ground state values of the exchange constants and related parameters.

With further heating towards $T_N \sim 640$ K, the spin-waves become heavily damped, as shown in Fig. 3 (d) and (e). The data taken at 580 K already show that although the scattered intensities are more intense around \mathbf{Q}_{AF} due to the dominating AFM correlations, well defined spin-waves are no longer present. While the Néel temperature marks the disappearance of static magnetic order in the system, the coherence of spin-wave excitations already diminishes at temperatures well below T_N .

In addition to probing the coherence of the spin-wave excitations, which are collective magnetic responses from the system, our neutron scattering measurements also provide information on the local spin structure around each Fe atom. The magnetic form factor $|F(\mathbf{Q})|^2$ describes the Fourier transformation of the spatial distribution of spin (density) around each magnetic ion (in our case, Fe³⁺), into momentum space. In Fig. 4 (b-d), we show the magnetic form factor for a Fe³⁺ ion with the blue solid lines. This magnetic form factor is isotropic and only depends on the length of \mathbf{Q} . However, recent analysis of inelastic neutron scattering data from high- T_C cuprates suggests²⁰ that the spin distribution around magnetic

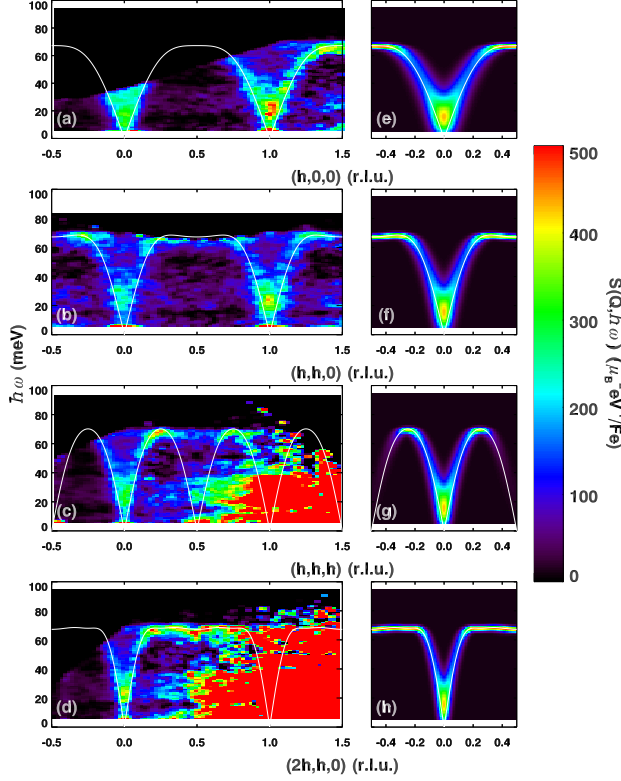


FIG. 2. (Color online) Magnetic excitations from BiFeO₃ at T=5 K. The vertical axes denote energy transfer, while the horizontal axes are $\mathbf{Q} - \mathbf{Q}_{\text{AF}}$ for \mathbf{Q} along [100], [110], [111], and [210] directions for (a), (b), (c) and (d), respectively. The strong background appearing at large \mathbf{Q} comes from phonon scattering. (e) to (h) are model calculations described in the text.

ions in metal oxides can be greatly affected by the presence of the oxygen ion, and could result in different effective magnetic form factors.

To compute the magnetic form-factor that includes the effects of the crystalline environment, a first principles Wannier analysis^{20,21} is employed. From LDA+U calculations of BiFeO₃^{22,23} the Fe is found to be in the high-spin $S = 5/2$ state. The magnetic form-factor is obtained by Fourier transforming the spin density of the low-energy Wannier functions of Fe. In Fig. 1 (b) and (c), we compare the atomic spin-density with the Wannier function derived spin-density. The main difference is that the Wannier function derived spin-density spreads into the neighboring oxygen atoms, which suppresses the magnetic form-factor at none-zero momenta. Direct comparison of the form factors are plotted in Fig. 4 (b)-(d). We can see that for most Q , the Wannier form factor is smaller than the previously used ionic form factor. An experimental verification of the new form factor is shown in Fig. 4 (a). Here we plot the ratio $R(\mathbf{Q}) = \frac{I(\mathbf{Q})/|F(\mathbf{Q})|^2}{I(\mathbf{Q}_0)/|F(\mathbf{Q}_0)|^2}$, where $I(\mathbf{Q})$ is magnetic scattering intensity measured at wave-vector \mathbf{Q} , while \mathbf{Q}_0 is the wave-vector equivalent to \mathbf{Q} in the first Brillouin zone. It is also worth noting that this type of calcu-

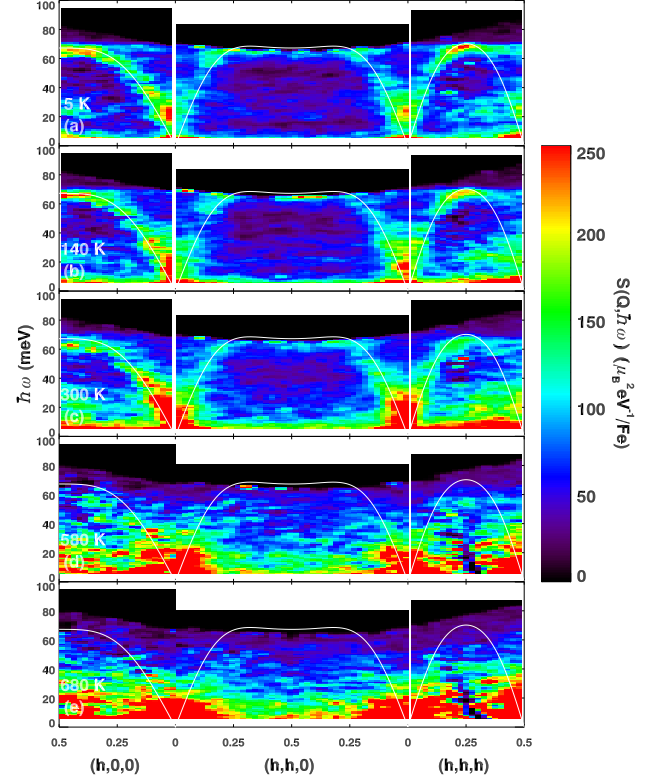


FIG. 3. (Color online) Magnetic excitations from BiFeO₃ measured at 5 K, 140 K, 300 K, 580 K, and 680 K. The horizontal axis denotes $\mathbf{Q} - \mathbf{Q}_{\text{AF}}$. The solid lines are dispersion calculated based on parameters obtained from the base temperature (5 K) data.

TABLE I. Parameters obtained from modeling the data at various temperatures. Note that in our spin Hamiltonian, one pair of spins \mathbf{S}_n and \mathbf{S}_m are counted twice, and their binding energy becomes $H_{nm} = J_{nm}(\mathbf{S}_n \cdot \mathbf{S}_m + \mathbf{S}_m \cdot \mathbf{S}_n) = 2J_{nm}\mathbf{S}_n \cdot \mathbf{S}_m$, so that the exchange constant J used here have same definition as those used in Ref. 12, but should be compared to half of the J values used in Ref. 13. The units are all meV except for the ordered moment $\langle M_z \rangle$, which is shown as multiples of μ_B .

	5 K	140 K	300 K	580 K	680 K
$\langle M_z \rangle$	3.9(2)	3.6 (2)	3.2 (3)	1.9 (4)	-
J_1	2.17(9)	2.17(9)	1.9(1)	1.5(2)	-
J_2	0.11(3)	0.11(3)	0.05(5)	0.03(9)	-
J_3	0.29(9)	0.29(9)	0.3(2)	0.2(3)	-
$2J_1\langle S_0 \cdot S_1 \rangle$	-21(1)	-21(1)	-18(1)	-12(2)	-
$2J_2\langle S_0 \cdot S_2 \rangle$	0.26(8)	0.26(8)	0.1(1)	0.1(2)	-
$2J_3\langle S_0 \cdot S_3 \rangle$	-2.8(8)	-2.8(8)	-3(1)	-2(2)	-
Γ	0	0	5 (2)	10(5)	-

lation is model (Hamiltonian) independent, and $R(\mathbf{Q})$ is supposed to always be 1 if the magnetic form factor used is correct. The results from the old ionic (blue symbols) and new Wannier (red symbols) magnetic form factors clearly suggest that the new form factor provides a better description of the \mathbf{Q} dependence.

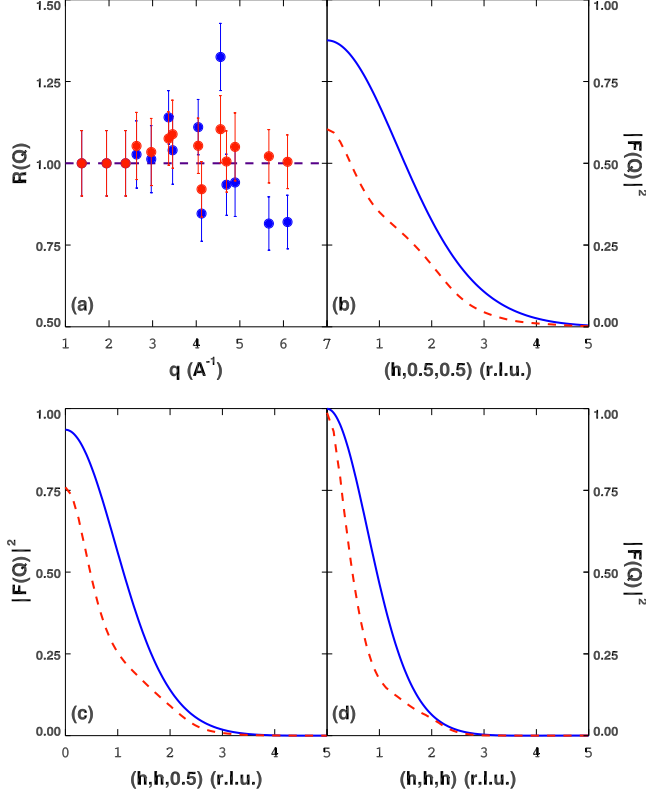


FIG. 4. (Color online) Comparison of the original ionic Fe form factor and the new Wannier form factor. (a) Plotting of the ratio $R(Q) = \frac{I(Q)/|F(Q)|^2}{I(Q_0)/|F(Q_0)|^2}$, where $I(Q)$ is magnetic scattering intensity measured at wave-vector Q , while Q_0 is the wave-vector equivalent to Q in the first Brillouin zone. Ideally this value should be 1 (see the dashed line). The red symbols are values calculated using the new Wannier form factor while the blue symbols using the old Fe ionic form factor. (b) to (d): $|F(Q)|^2$ plotted along different directions.

Using this hybrid magnetic form factor, the ordered moment per Fe at various temperatures is calculated and listed in the first row of Table I. At $T=5$ K, this value $M_z = 4 \mu_B$ corresponds to $S_z = 2.0$, consistent with the moment obtained from other measurements^{24,25}, and close to the theoretical limit of $S_z = S = 5/2$, using a g -factor of 2. Frustration due to a positive (AFM) J_2 is likely the main reason for the difference. We can also obtain an integrated spectral weight from all the spin-wave excitations, to be $S_{dynamic} \sim 2.5$ (i.e. $M_{dynamic}^2 = S_{dynamic} g^2 \mu_B^2 = 10 \mu_B^2$). Combining the two we have a total squared moment of $M^2 = M_z^2 + M_{dynamic}^2 = 16 + 10 = 26 \mu_B^2$, which is supposed to be $S(S+1)g^2 \mu_B^2$ to satisfy the sum rule (see Methods). This corresponds to $S \sim 2.1$ per Fe, in good agreement with the expected $S = 5/2$ from Fe^{3+} . On the other hand, if a simple Fe^{3+} magnetic form factor were used, we would have obtained a $S_z = 1.4$ and $S = 1.4$ instead, which are much lower than the expected values.

Overall, our work demonstrates that the electromagnon excitations in $BiFeO_3$ can be very well modeled with a simple spin-wave model from a G-type AFM at low temperature. Despite the cycloid modulation induced by coupling to the electric polarization, most of the spin dynamics are barely modified, and consistent with the behaviour of a conventional spin-wave. Upon heating decoherence of spin-wave excitations starts to occur even at just below room temperature (300 K). At 580 K which is well below T_N , the coherence mode is already almost completely destroyed. In addition, a strong hybridization between the Fe and O orbitals needs to be taken into account when the magnetic response is considered. Even as a good insulator, the electrons responsible for the magnetic moments are not restricted at the Fe sites, and the local magnetic moment could extend well beyond the typical ionic radius of Fe^{3+} into the adjacent O^{2-} sites.

I. METHODS

Single crystal samples of $BiFeO_3$ are grown by floating zone technique at BNL. The crystal used in the measurement has a cylindrical shape, and weighs about 3.5 g, with a mosaic less than 2 degrees. Inelastic neutron scattering experiments are performed on the ARCS time-of-flight spectrometer at the Spallation Neutron Source (SNS) at Oak Ridge National laboratory. Incident energies of 60 meV and 120 meV are used to probe the lower and higher part of the spin excitation.

The spin-wave calculations are based on a classical spin-wave model assuming a $S = 5/2$ G-type AFM²⁶. Based on the model, the values of J_1 , J_2 , and J_3 can all be directly derived from the data if the energies of the spin-wave excitations can be accurately determined at each wave-vector. For instance, if we define $Q_1 = Q_{AF} + (0.25, 0.25, 0)$, $Q_2 = Q_{AF} + (0.25, 0.25, 0.25)$, $Q_3 = Q_{AF} + (0.5, 0.25, 0)$, based on a simple spin-wave calculation, we have $J_1 = \frac{1}{4S}(E_2^2 - E_1^2)^{1/2}$, $J_2 = \frac{1}{8S}(E_2 - E_3)$, and $J_3 = \frac{1}{4}(\frac{E_3}{4S} - 3J_1 + 8J_2)$. Here E_1 , E_2 , and E_3 are spin-wave energies at Q_1 , Q_2 , and Q_3 , respectively.

After normalizing the data using phonon intensities which have been obtained from the same measurements, a sum rule applies: $\int_{BZ} \int S(Q, \hbar\omega) d^3Q d(\hbar\omega) / \int_{BZ} d^3Q = S(S+1)$, where $S(Q, \hbar\omega)$ is the dynamic spin correlation function, and the integral is performed in one Brillouin zone. In our case $I(Q, \hbar\omega) = \frac{2}{3}S(Q, \hbar\omega)$, where $I(Q, \hbar\omega)$ is the normalized intensity. The factor $\frac{2}{3}$ arises from assuming an isotropic dynamic spin correlation function (i.e. $S^{xx} = S^{yy} = S^{zz}$), and averaging the polarization factor of different domains. The scattering intensity can be modeled with the single mode approximation (SMA)²⁷, and the parameters that can vary include the exchange parameters J_1 , J_2 , J_3 , ground state binding energies for the nearest, second nearest (face diagonal), and third nearest (body diagonal) spin pairs, $2J_1\langle S_0 S_1 \rangle$, $2J_2\langle S_0 S_2 \rangle$, $2J_3\langle S_0 S_3 \rangle$, and a finite energy broadening Γ for high temperature data.

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